Study of optical absorbance in porous silicon nanowires for photovoltaic applications

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ABSTRACT: Porous silicon nanowires (*P*SiNWs) layers fabrication was reported. Reflectance spectra were measured as a function of the nanowire length and were inferior to 0.1% and a strong photoluminescence (PL) signal was measured from samples. Models based on cone shape of nanowires located in circular and rectangular bases were used to calculate the reflectance using the Transfert Matrix Formalism (TMF) of *P*SiNWs layer. The modeling of the reflectance permits to explain this value by taking account into the shape of the nanowires and its porosity. Optical absorbance and transmission were also theoretically studied. The absorbance was superior to that obtained with silicon nanowires and the ultimate efficiency was about equal to 25% for normal incidence angle. These results could be applied to the potential application in low-cost and high efficiency *P*SiNWs based solar cells.

I. INTRODUCTION

Various types of solar cell, such as silicon-based (crystalline, amorphous, and microcrystalline),[1] GaAs,[2] and organic cells[3] have recently been developed. Crystalline-silicon (c-Si) solar cells are predominantly used for photovoltaic power generation due to their high photovoltaic conversion efficiency, long-term stability, and optimized manufacturing process.[4] Recently there has been significant interest in the photovoltaic properties of nanostructured materials such as quantum dots[5,6] and nanowires (NWs)[7- 9] for the development of higher efficiency and cost-effective solar cells. NW-based photovoltaic structures, in particular, provide potential advantages for more efficient charge collection due to radial junction structure through their cylindrical geometry[10] and the benefits of a natural anti-reflective structure that allows enhanced light trapping and absorption.[11]

In particular, silicon nanostructures have been investigated for their potential use in cost-effective-third-generation high efficiency solar cells due to their unique optical and electrical characteristics.[11-16] Silicon Nanowires (SiNWs) arrays vertically aligned to the substrate demonstrate broadband optical absorption due to strong light trapping by multiple scattering of the incident light and the optical antenna effect. The optical properties are affected principally by geometric factors of SiNW such as wire diameter, length and periodicity. Several methods have been reported for synthesizing SiNWs, including chemical vapor deposition (CVD),[17] laser ablation,[18] physical vapor deposition (PVD),[19]... Among these, wet electroless etching[20-22] has been widely used as an alternative top-down route in the cell fabrication process.

Recently, Porous Silicon nanowires (*P*SiNWs) have been developed, notably numerous studies have been realized on the synthesis and their physical properties[10-13, 23] using metal assisted chemical etching method.

In this paper, *P*SiNWs are studied experimentally by measuring the photoluminescence, reflectance and numerically by introducing the effect of the nanowire shape, porosity, and by analysing the *P*SiNWs optical absorption, transmittance and reflectance with regards to the results obtained from silicon thin films and SiNWs for photovoltaic applications.

II. EXPERIMENTS

*P*SiNWs were fabricated by Ag assisted chemical etching method from an n-type Si wafer (100) with a resistivity of 0.01-0.02 Ω-cm. The Si wafers were cleaned using acetone followed by ethanol for 5 minutes in an ultrasonic bath. Next, the wafers were immersed in a piranha solution H_2SO_4/H_2O_2= (3:1) for 20 minutes to remove the organic deposits from the surface. The cleaned wafers were transferred into $HF/AgNO_3$ solution with a concentration of 4.8 M/0.005 M for Ag-deposition, followed by rinsing with de-ionized water to remove extra silver ions. Then, the Si samples were etched in the HF 4.8M/0.5M H_2O_2 solution for different times. At the end, samples were rinsed again for 10 minutes with HNO_3 solution to dissolve the Ag metal nanoparticles.[23]

The surface morphology of *P*SiNWs was investigated using a FEI's Magellan 400 FEG SEM operating at 30 keV beam energy. The crystal structure, size of Si crystallites, and the average pore size were measured using the FEI's TitanG^2 80-300 TEM. The photoluminescence (PL) measurements were performed at room temperature using the Jobin Yvon LabRAM ARAMIS system. A 8 mW diode-pumped solid-state (DPSS) laser emitting at 473 nm was used as the PL excitation source.

Otherwise, the reflectance spectra of the *P*SiNWs were studied by a LAMBDA 900 Perkin-Elmer beam spectrometer equipped with a specular reflectance module with a 6° fixed angle.

III. RESULTS AND DISCUSSIONS

Nanowires formed can have rough or smooth surfaces depending on the catalyst type and etching conditions. Figure 1 (a) show the formation of nanowires by diffusion of AgNPs (inset) inside Si substrate. Ag^+ catalyzes the dissolution of Si through the formation of SiF_6^{2-}. It is apparent that the transport of Ag^+ is isotropic while the AgNPs merely drop downwards. Hence, the AgNPs facilitated the nanowire formation through vertical chemical etching, while the isotropic diffusion of Ag^+ promoted lateral chemical etching and pore formation.[23]

After HNO_3 treatment to remove the Ag metal nanoparticles, the top view image (Fig. 1(b)) shows an example of the vertically oriented *P*SiNWs with tips of NWs congregates together and the diameter of the congregated bundles is several micrometers (inset). These congregated bundles are uniformly distributed on the entire samples and confirmed from the cross-section images. The mean diameter of wires was about 250 nm and different lengths (10 µm, 13 µm, 28 µm, and 31 µm) of samples were fabricated by changing the etching time. The physical characteristic of the PSiNWs can be found elsewhere in ref. 23. Figure 1 (c) shows the Energy filtered TEM (EFTEM) analysis of nanowires. It is noted that mesopores are mostly found near the top of the nanowires with an average pore size between 10 and 40 nm.

Optical properties of the PSiNWs samples have been investigated using PL spectroscopy. It is known that the mesoporous silicon nanostructure gives rise to strong visible emission.[24] Figure 2 shows the PL spectra of the samples etched with HF concentration of 4.8 M with H_2O_2 concentration of 0.005 M. It is observed that the asymmetric PL spectra have two dominant peaks around 700 and 760 nm. The highest PL peak at 760 nm is related to the emission from Si–O bond.[24, 25] After HNO_3 and HF treatments for 5min to remove the oxide, all samples show similar PL peak wavelength at 800 nm. However, samples without HF treatment show a

significant blue-shift with PL wavelength peak at 700 nm. This blue-shift and increase of PL intensity have been attributed to the presence of defect states in Si-Ox.[23] This has been correlated to the red shift of PL spectrum that suggests the interfacial between Si and surface oxide, as well as the quantum confinement effect, plays a critical role in the light emission process.[23]

Moreover, Figure 3 (a) shows the experimental spectra of PSiNWs samples. These spectra reveal the very low reflectance of PSiNW layers, inferior to 0.1%, and permit to use these layers as anti-reflection coating of solar cells. Moreover, the reflectance decreases as the layer thickness increases. Notably, the measured reflectance values are lower than those obtained for SiNW array.[26] To study the theoretically spectra, the generic structure under investigation is schematically depicted in Figure 3 (b). The PSiNWs were simulated by Si cones.[27, 28] The z-axis is perpendicular to the Si substrate surface. The bottom of the PSiNWs is at $z = 0$ and the top at $z = h$. The radius of the PSiNW depends on the z-position by the following equation $\rho = \frac{h - z}{h}$ where R is the radius of the cone circle and h the thickness of layer. The PSiNW is divided into n horizontal layers with the same thickness denoted d equal to 1 nm. In the simulation model, each PSiNW is supposed to be located in a rectangular of edge equal to a or in a circle of diameter equal to a. According to the porosity value near of 50%, a is chosen as $2R$. This permits to simulate the reflectance for two different volume shapes and to take the complex shape of PSiNWs into account. The transfer matrix formalism (TMF) was used to calculate the reflectance, transmittance and absorbance of PSiNWs arrays. The absorbance was given by $A(\omega) = 1 - R(\omega) - T(\omega)$. With this TMF, the Bruggeman model was used to calculate the refractive index of PSiNWs layer. From the Bruggeman model,[29, 30] knowing the volume fraction of Si and void, the refractive index of PSiNWs layer was deduced. Theoretical reflectance spectra of PSiNWs on silicon substrate corresponding to different samples with their thickness

by considering cone shape are reported in Fig. 3(b). The interferences are clearly observed in the calculated reflectance for the low lengths of PSiNWs whereas the experimental reflectance shows no interference. However, the same trends are observed on experimental and theoretical spectra: the experimental value of reflectance is between those obtained by the two models. The reflectance decreases strongly for the low wavelength and increases slightly towards the higher wavelengths. According to the used model, the porosity is majored or minored with a circle base or rectangular base respectively that is why the reflectance values are different.

Figures 4 compare the reflectance, transmittance, and absorbance of PSiNWs by using the two models with rectangular or circular base. Three lengths were selected to show the thickness dependent absorption. The spectra of silicon thin film with the same thickness are also plotted in the same figures as references. As the thickness increases, the PSiNW absorbance increases as for the bulk silicon thin films. However, when wavelength decreases, absorbance of PSiNWs rises and reaches a plateau region shared by all lengths close to 100%. At these wavelengths, the absorbance for nanowires whatever the considered thickness is much higher than that of the Si bulk. The width of plateau region and the absorbance value increase as the PSiNWs thickness increases. We note that these absorbance values are close to 100 % and are higher than those obtained from references [26, 27] for silicon nanowires. While in the higher wavelengths, the absorption in the film is more efficient. To understand the trends of absorption in PSiNWs, reflectance and transmittance are plotted for different lengths of PSiNWs and for Si thin film for the same thickness. The reflectance is much lower than those obtained of Si thin film throughout the entire spectral region. When the wavelength decreases, the reflectance tends toward a low value near to 0 corresponding to the plateau observed for the absorbance spectrum and for each

film thickness. The reflectance values are lower than those measured on silicon nanowires due to the shape of nanowires[26-28] and the porosity of the wires. We notice that for higher wavelength, interference effects exist as observed in Fig. 3 (a) because the extinction coefficient of silicon is small. Furthermore, It is the same trend for transmittance spectra by zooming at high wavelengths. Meanwhile, PSiNWs transmittance is higher than Si thin film in the considered wavelength range and approaches to zero in the low wavelengths. Therefore, in low wavelength range, the very low reflectance and the zero transmittance of PSiNWs lead to higher absorbance compared to Si thin film and also SiNWs, near to 100% at these wavelengths. Lastly, the transmittance and reflectance values decrease as the thickness increases.

To evaluate the overall absorption performance of PSiNWs, the ultimate efficiency using the Air Mass 1.5 direct normal and circumsolar spectrum[31] was calculated. It is given by the following equation[32]: $\eta = \frac{\int_{310nm}^{\lambda_g} I(\lambda)A(\lambda)d\lambda}{\int_{310nm}^{4000nm} I(\lambda)d\lambda}$; where λ is wavelength, $I(\lambda)$ is the spectral irradiance (power density) of the ASTM AM1.5 direct normal and circumsolar spectrum, $A(\lambda)$ is the absorbance and λ_g=1127 nm is the wavelength corresponding to the 1.1 eV band gap of bulk silicon.

Figure 5 (a) shows the absorbance of *P*SiNWs as a function of incidence angle. The absorbance increases with the incidence angle due to the increasing to optical path. In fig. 5 (b), the efficiency is plotted versus incidence angle for *P*SiNWs with 30 µm thickness compared to Si thin film with the same thickness. The efficiency of *P*SiNWs tends to be higher than that obtained by Si thin film. Furthermore, the efficiency can be improved by using light trapping to

increase optical path.[26] We can notice that the efficiency values are higher than those obtained by SiNWs arrays.[26]

IV. CONCLUSION

The elaborated *P*SiNWs permits to obtain a very low reflectance that increases with layer thickness. A strong photoluminescence (PL) signal has been measured from samples. The reflectivity of the samples decreased drastically compared to Si substrate. This low value is explained by the conic shape of the nanowires and their porosity between the nanowires but also by the porosity of the nanowires. The calculated absorbance shows a plateau near to 1 for the low wavelengths because of this low reflectance and the ultimate efficiency is higher (25%). Finally, our work demonstrates the feasibility to use *P*SiNWs fabricated by Ag assisted chemical etching method in heterojunction thin film solar cells with promising antireflective performance. Moreover, the important specific surface of these nanostructures can also be potentially useful as antireflection layers for photovoltaic applications but also as optical sensors. [33, 34]

[1] I. P.Wurfl, X. Hao, A. Gentle, D. H. Kim, G. Conibeer, M. A. Green, *Appl. Phys. Lett.*, **95** (2009), p 153506.

[2] J. Wu, D. Shao, Z. Li, M. O. Manasreh, V. P. Kunets, Z. M. Wang, G. J. Salamo, *Appl. Phys. Lett.*, **95** (2009), p 071908-1.

[3] X. Chen, J. Yang, J. Lu, K. K. Manga, K. P. Loh, F. Zhu, *Appl. Phys. Lett.*, **95** (2009), p 133305-1.

[4] J. Lee, N. Lakshminarayan, S. K. Dhungel, K. Kim, J. Yi, *Solar Energy Materials & Solar cells,* **93** (2009), p 256.

[5] A. Martı´, N. Lo´pez, E. Antolın, E. Ca´novas, C. Stanley, C. Farmer, L. Cuadra, A. Luque, *Thin Sol. Films*, **511** (2006), p 638.

[6] Q. Shao, A. A. Balandin, A.I. Fedoseyev, M. Turowski, *Appl. Phys. Lett.*, **91** (2007),p 163503.

[7] M. Law, L. E. Greene, J. C. Johnson, R. Saykally, P. Yang, *Nat. Mater.*, **4** (2005), p 455.

[8] J. R. Maiolo III, B. M. Kayes, M. A. Filler, M. C. Putnam, M. D. Kelzenberg, H. A. Atwater, N. S. Lewis, *J. Am. Chem. Soc.*, **129** (2007), p 12346.

[9] T. Stelzner, M. Pietsch, G. Andra¨, F. Falk, E. Ose, S. Christiansen, *Nanotechnology*, **19** (2008), p 295203.

[10] B. M. Kayes, H. A. Atwater, N. S. Lewis, *J. Appl. Phys.*, **97** (2005), p 114302.

[11] L. Hu, G. Chen, *Nano Letters*, **7** (2007), p 3249.

[12] Y. Hwang, A. Bukai, and P. D. Yang, *Nano Lett.* **9** (2009), p 410.

[13] E. Garnett, and P. D. Yang, *Nano Lett.*, **10** (2010), p 1082.

[14] C. Lin, and M. L. Povinelli, *Opt. Express*, **22** (17) (2009), p 19371.

[15] A. Najar, J. Charrier, H. Ajlani, N. Lorrain, S. Haesaert, M. Oueslati, and L. Haji, *Mat. Scie. Eng. B*, **146** (1) (2008), pp 260-263.

[16] A. Najar, H. Elhouichet, N. Lorrain, and M. Oueslati, *Appl. Surf. Scie.***,** ***256*** *(*16) (2006), pp 5808-5813.

[17] O. Gunawan, S. Guha, *Solar Energy Materials & Solar Cells*, **93** (2009), p 1388.

[18] A. M. Morales, C. M. Lieber, *Science*, **279** (1998), p 208.

[19]L. Schubert, P. Werner, N. D. Zakharov, G. Gerth, F. M. Kolb, L. Long, U. G¨osele, T. Y. Tan, *Appl. Phys. Lett.*, **84** (2004), p 4968.

[20] D. Kumar, S. K. Srivastava, P. K. Singh, M. Husain, V. Kumar, *Solar Energy Mat. and Solar Cells*, **95** (2011), p 215.

[21] H. Li, R. Jia, C. Chen, Z. Xing, W. Ding, Y. Meng, D. Wu, X. Liu, T. Ye, *Appl. Phys. Lett.*, **98** (2011)**,** p 151116.

[22] A. Najar, M. Gerland, and M. Jouiad, *J. Appl. Phys.* **111** (9) (2012), p 093513-5.

[23] A. Najar, A. B. Slimane, M. N. Hedhili, D. H. Anjum, T. K. Ng, and Boon S. Ooi, *J. of Appl. Phys.***112** (2012), p 033502.

[24] A. G. Cullis, L. T. Canham, and P. D. J. Calcott, *J. Appl. Phys.* **82**, (1997) p 909.

[25] L. Lin, S. Guo, X. Sun, J. Feng, and Y. Wang, *Nano. Res. Lett.* **5**, (2010) p1822.

[26] L. Hu and G. Chen, *Nano Lett.* **7** (2007), p 3249.

[27] T-H. Pei, S. Tiyagu, and Z. Pei, *Appl. Phys. Lett.* **99** (2011), p 153108.

[28] A. Najar, J. Charrier, P. Pirasteh, and R. Sougrat, *Opt. Exp.* **20** (15) (2012), p 16861.

[29] D. E. Aspnes, *Thin Solid Films* **89** (1982), p 249.

[30] W. Theiss, *Surf. Sci. Reports* **29** (1997), pp 91–93 and 95–192.

[31]ASTM, "Reference Solar Spectral Irradiance: Air Mass 1.5 Spectra," *http://rredc.nreal.gov/solar/spectra/am1.5*.

[32] W. Shockley, and H. J. Queisser, *J. Appl. Phys.* **32** (3) (1961), p 510.

[33] G. Zheng, F. Patolsky, Y. Cui, W. U. Wang, and C. M. Lieber, *Nat. Biotechnol.* **23** (2005), p 1294.

[34] J. Charrier and M. Dribek, *J. Appl. Phys.* **107** (4) (2010), p 44905-1.

FIGURES CAPTIONS

FIG. 1. (a)-(c) Cross-section micrographs of PSiNWs before and after HNO_3 treatment, respectively. (b) Top view SEM micrograph of PSiNWs after HNO_3 treatment, and (c) TEM observation of nanowires.

FIG. 2. PL spectra of PSiNWs (a) without and (b) with HF treatment, respectively.

FIG. 3. (a) Experimental reflectance spectra and theoretical reflectance spectra using the conic model with circular base and rectangular base for the different thicknesses of samples (10 µm, 13 µm, 28 µm, and 31 µm). (b) Schematic representation of SiNWs and effective multilayer structure with cone shape and TEM image showing the cone shape.

FIG. 4. (a)-(b), (d)-(e), and (g)-(h) are the absorbance, reflectance and transmittance spectra of PSiNW for 5 and 10 µm respectively by considering circular base and rectangular base. The optical properties of silicon thin film are plotted for comparison. (c), (f) and (i) are the absorbance, reflectance and transmittance spectra of PSiNW for different thicknesses (5, 10 and 31µm) respectively by considering circular base and rectangular base.

FIG. 5. (a) Absorbance spectra of PSiNW with a thickness equal to 30 µm for different incidence angle (in degree). Inset: The ASTM Air Mass 1.5 direct and circumsolar spectrum from ref. 19. (b) Ultimate efficiency as a function of the incidence angle for TE polarization and for a 30-µm thick PSiNW film.